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R&T Code 4131D02

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Technical Report No. 81

Investigation of Anomalous Predicted Bond Lengths in Some 1,1-Difluorohydrazines

by

Peter Politzer and M. Edward Grice

Prepared for Publication

in

Journal of Chemical Research

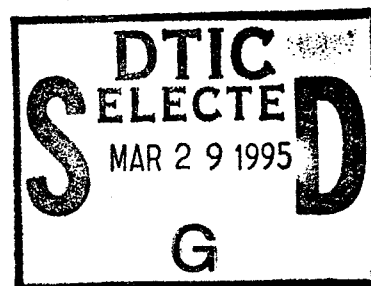
Department of Chemistry
University of New Orleans
New Orleans, LA 70148

March 20, 1994

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REPORT DOCUMENTATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 20, 1995		3. REPORT TYPE AND DATES COVERED Preprint of article	
4. TITLE AND SUBTITLE Investigation of Anomalous Predicted Bond Lengths in Some 1,1-Difluorohydrazines				5. FUNDING NUMBERS N00014-95-I-0028 Dr. Richard S. Miller R&T Code 4131D02	
6. AUTHOR(S) Peter Politzer and M. Edward Grice				7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of New Orleans Department of Chemistry New Orleans, Louisiana 70148	
8. PERFORMING ORGANIZATION REPORT NUMBER 81				9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Code 333 800 N. Quincy Street Arlington, VA 22217	
10. SPONSORING / MONITORING AGENCY REPORT NUMBER				11. SUPPLEMENTARY NOTES By _____ Distribution / _____	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release. Unlimited distribution				12b. DISTRIBUTION CODE Availability Codes Dist Avail and/or Special A-1	
13. ABSTRACT (Maximum 200 words) Bond length anomalies found in some 1,1-difluorohydrazines are conformation-dependent and are absent in the presence of strongly electron-attracting substituents, supporting their interpretation in terms of charge delocalization.					
14. SUBJECT TERMS 1,1-difluorohydrazines; bond length; electron-attracting; charge delocalization; conformation dependent				15. NUMBER OF PAGES 7	
16. PRICE CODE				17. SECURITY CLASSIFICATION OF REPORT Unclassified	
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		20. LIMITATION OF ABSTRACT Unlimited	

INVESTIGATION OF ANOMALOUS PREDICTED BOND LENGTHS IN SOME 1,1-DIFLUOROHYDRAZINES

Peter Politzer* and M. Edward Grice

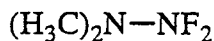
Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, USA

Abstract

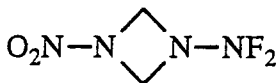
Bond length anomalies found in some 1,1-difluorohydrazines are conformation-dependent and are absent in the presence of strongly electron-attracting substituents, supporting their interpretation in terms of charge delocalization.

Introduction

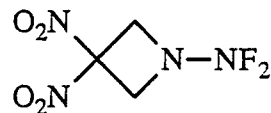
In a recent computational study of the 1,1-difluorohydrazines **1** - **3**,¹ our optimized ground state geometries revealed the interesting features that (a) one N-F bond is considerably longer than the other, and (b) the N-N distances are shorter than anticipated. The relevant data are summarized in Table 1; they were obtained by a density functional procedure using the Gaussian 92/DFT code,² with the Becke exchange³ and Perdew correlation⁴ functionals and a 6-31G** basis set. It was verified, by the absence of negative vibration frequencies, that these geometries correspond to local energy minima.⁵ Also included in Table 1, for reference purposes, are computed bond lengths for $\text{H}_3\text{C}-\text{NF}_2$ and $(\text{H}_3\text{C})_2\text{N}-\text{NH}_2$. These shall be viewed as being reasonably typical values for these bonds, within the framework of the computational approach.



1



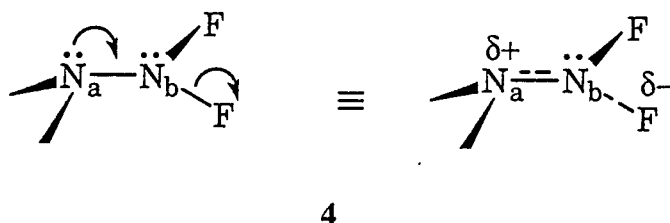
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* Author to whom correspondence should be addressed.

In the molecules **1** - **3**, one N-F bond has a length very similar to those in $\text{H}_3\text{C}-\text{NF}_2$, while the other is at least 0.1 Å longer. On the other hand, the N-NF₂ bonds are more than 0.1 Å shorter than in $(\text{H}_3\text{C})_2\text{N}-\text{NH}_2$. We suggested in our earlier paper that these features reflect a delocalization of electronic charge such as is depicted in **4**:¹



This delocalization, which can be viewed as an example of the anomeric effect,⁵⁻⁸ is presumably most effective if the lone pair on N_a is concentrated in the same plane as the N-N and one of the N-F bonds; thus one of the latter is lengthened but not the other. (An extended discussion of the nitrogen lone pairs in some 1,1-dimethylhydrazines has been presented by Murray *et al.*⁹)

Results and Discussion

In an effort to better understand the electronic and structural factors in these molecules, we investigated the effects of rotating the NF₂ portion of **1** around the N-N bond. Using the computational procedure described above, the geometry was re-optimized at 60° intervals relative to the completely eclipsed conformation, **1A**. On this basis, the ground state, **1C**, corresponds to a rotation of 69.9°. The results are shown in Figure 1.

The most striking situations are found in **1B** and **1D**. In **1B**, the lone pair on N_a is exactly coplanar with the N-F_a bond. The latter is consequently greatly elongated, to 1.564 Å, while the N-F_b is a normal 1.422 Å. In **1D**, after a rotation of 60°, the lone pair of N_a is coplanar with the N-F_b bond, and now the latter is the one that is anomalously long, 1.505 Å, and the N-F_a is normal, at 1.432 Å. In both conformations, the N-N bond is considerably shortened, to the 1.36 Å - 1.38 Å range; this is about 0.12 Å less than in $(\text{H}_3\text{C})_2\text{N}-\text{NH}_2$. The computed ground state, **1C**, is quite similar to **1B**.

In **1A** and in **1E**, on the other hand, the lone pair on N_a affects both N–F bonds equally; thus both have the same length. The N–F and the N–N distances in **1A** and **1E** are all intermediate between their extreme values in **1B** and **1D** and their normal ones in H_3C-NF_2 and $(H_3C)_2N-NH_2$. This indicates that some delocalization of charge is occurring, but not to the same extent as when the N_a lone pair is coplanar with an N–F bond.

As would be anticipated, the highest energy conformation is **1A**, in which the two lone pairs eclipse each other. The completely staggered (*anti*) conformation **1E**, in which the lone pairs are at their maximum separation, is higher in energy than either **1B** (*gauche*) or **1D**; this presumably reflects the greater degrees of delocalization in the latter two, and the resulting stabilization.

The results presented in Figure 1 are consistent with the charge delocalization depicted in structure **4**, which is proposed as an interpretation of the bond length anomalies observed in **1** - **3**. While we have shown that these molecules do have energy minima, the presence of the elongated N–F bond in each of them reinforces concern regarding a possible facile loss of fluoride ion.¹⁰ This could be a source of difficulties in synthesis. It was suggested by Baum¹¹ that this problem could perhaps be avoided or diminished by having electron-attracting substituents on N_a , which would have the effect of opposing the charge delocalization shown in **4**.

We have accordingly investigated the structure of $(NC)_2N-NF_2$, in which two cyano groups have been substituted on N_a ; these are known to be strongly electron-withdrawing through induction.¹² The geometry was optimized at the Gaussian 92/DFT/B-P86/6-31G** level, and was verified to correspond to an energy minimum. The consequences of introducing the cyano groups are quite pronounced. The bonds around N_a become essentially coplanar, in contrast to their distinctly pyramidal arrangements in **1** - **3**. The N–F bond lengths are now nearly the same and are quite normal, 1.410 Å and 1.420 Å, as is the N–N, 1.460 Å (Table 1). Thus the anomalies found in **1** - **3** have been eliminated; the anomeric effect is not observed in $(NC)_2N-NF_2$.

These findings provide further support for our interpretation of these anomalies in terms of

4. They also offer some encouragement concerning the feasibility of synthesizing compounds of the type $R_aR_bN-NF_2$, in which R_a and R_b are strongly electron-attracting.

Acknowledgements

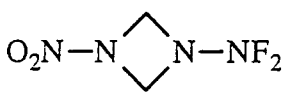
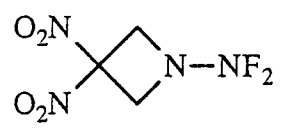
We thank Drs. K. Baum, J. H. Boyer, J. S. Murray, A. G. Stern and M. L. Trudell for very helpful discussions and suggestions, and we express our appreciation for the support provided by the Office of Naval Research through contract no. N00014-95-1-0028.

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Table 1. Computed bond lengths.^a

Molecule		Bond	Length (Å)
(H ₃ C) ₂ N—NF ₂	1	N—F	1.431, 1.542
		N—N	1.358
	2	N—F	1.418, 1.536
		N—NF ₂	1.368
	3	N—F	1.417, 1.538
		N—N	1.366
H ₃ C—NF ₂		N—F	1.436, 1.436
(H ₃ C) ₂ N—NH ₂		N—N	1.492
(NC) ₂ N—NF ₂		N—F	1.410, 1.420
		N—N	1.460

^aReference 1; obtained by density functional Gaussian 92/DFT/B-P86/6-31G** calculations.

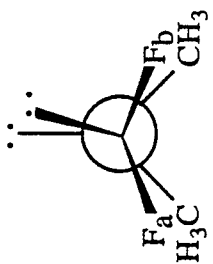
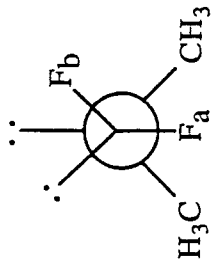
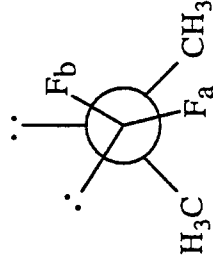
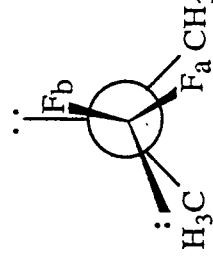
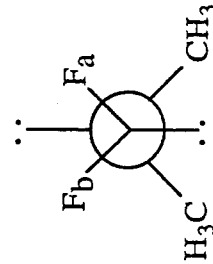
					
Angle of rotation (deg)	0	60	69.9	120	180
Relative energy (kcal/mole)	13.1	0.4	0.0	7.9	8.9
N-F _a length, Å	1.493	1.564	1.542	1.432	1.464
N-F _b length, Å	1.493	1.422	1.431	1.505	1.464
N-N length, Å	1.421	1.362	1.358	1.376	1.423

Figure 1. Calculated properties of conformers of $(\text{H}_3\text{C})_2\text{N}-\text{NF}_2$ produced by rotation around N-N bond. The lone pairs on the two nitrogens are included in the Newman projections. **1A** and **1D** represent completely eclipsed conformations; **1C** is the ground state.